The P-States of Systems of Three Coulombic Particles

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ABSTRACT

Center-of-mass coordinates are employed to determine the dependence of energy and other physical properties of systems with three Coulombic particles (two identical) on the masses of the particles. No adiabatic approximation is needed, since the non-relativistic and spin free Hamiltonian with the exact mass dependence is used in the variational problem. The total angular momentum of the particles is quantized to unity. Both symmetry states with the space-z-component of angular momentum $M_z = 0$ are considered. The computations cover the entire range of the mass ratio as well as several different charges of the particles. In most cases the energies obtained are either the lowest yet found or the first to be reported.

I. INTRODUCTION

Over the past few years there have appeared several papers on the quantum mechanical three-body problem in which the exact dependence of the Hamiltonian on the masses has been properly taken into account.[1-7] The interest in this problem has been aroused by the need for a more direct approach in describing a system of three particles of nearly equal masses, since the usual approximation of infinitely heavy (stationary) nuclei obviously cannot be made. If all the particles are to be allowed to move the nonrelativistic and spin free Hamiltonian of the system is expressed in terms of center-of-mass coordinates, and the Schrödinger equation becomes separable into two parts, the one describing the motion of the particles around the center of mass being the only one of interest here. All the work done so far has been on the ground states of molecular-like systems (the paper by Kolos, et al, with its treatment of the ground state of atomic helium being the only exception). For zero angular momentum states the wavefunctions depend only on the relative configuration of the particles, i.e. they are independent of the orientation in space. This fact leads immediately to a considerable simplification of the algebra of the problem. However, states with higher rotational quantum number do depend on the orientation in space, and the problem becomes correspondingly more difficult. It is the purpose of this work to investigate systems of three Coulombic particles (two identical) of

arbitrary masses in a state with rotational quantum number equal to unity. The coordinate transformation and the resulting Hamiltonian are the subject of Section II. Section III is devoted to the choice of wavefunctions. Results for all investigated systems are presented and discussed in Sections IV and V, respectively. Finally, the isotope shifts for some atomic ions are considered in Section VI.

II. COORDINATES, HAMILTONIAN, AND UNITS

The Schrödinger equation for a system of N particles is

$$\left(-\tfrac{1}{2}\hbar^2 \sum_{i=1}^{N} (1/m_i)\nabla_i^2 + V \right) \psi = E_T \psi, \qquad \text{(II-1)}$$

where V is the interparticle potential energies, m_j is the mass of the jth particle, and the differentiation is with respect to the laboratory coordinates x_j, y_j, z_j. The coordinates of the kth particle may be eliminated by the transformation

$$X = (1/M) \sum_{i=1}^{N} m_i x_i,$$

$$x_j' = x_j - x_k, \qquad \text{(II-2)}$$

where

$$M = \sum_{i=1}^{N} m_i, \qquad \text{all } j \neq k,$$

in favor of the center of mass coordinates X, Y, Z. When Eqs. (II-2) are substituted into Eq. (II-1) the resulting Schrödinger equation may be separated into a part describing the translational motion of a free particle of mass M and energy E_C, and another part describing the internal motion of the N particles. The internal Schrödinger equation is[8]

$$\left[-\tfrac{1}{2}\hbar^2 \left(\sum_{i\neq k}^{N} (1/m_i)\nabla_i'^2 + (1/m_k) \sum_{i,j\neq k}^{N} \nabla_i' \cdot \nabla_j' \right) + V \right] \psi$$

$$= E\psi, \tag{II-3}$$

where $E = E_T - E_C$ and the differentiation is with respect to the relative primed coordinates defined by Eq. (II-2). In the present case the numbering has been chosen such that the two identical particles are labeled 1 and 2 while the odd particle is referred to as 3. It is convenient to adopt the units

$$\epsilon = \mu e^4 \hbar^{-2} \text{ for energy}$$

and

$$a_0 = \hbar^2 \mu^{-1} e^{-2} \text{ for length,}$$

where μ is the reduced mass,[9]

$$\mu = mm_3/(m + m_3), \qquad m = m_1 = m_2.$$

Also, let the mass ratio be

$$\rho = m/m_3,$$

so that

$$\mu = m/(1 + \rho).$$

If the third (odd) particle is chosen to be the one to which the other two will be referred as origin, the internal Hamiltonian for the system under consideration becomes

$$H = -\tfrac{1}{2}(\nabla_{31}^2 + \nabla_{32}^2) - \rho(\rho + 1)^{-1}\underset{\sim}{\nabla}_{31}\cdot\underset{\sim}{\nabla}_{32} + V, \qquad \text{(II-4)}$$

where, in accordance with Eq. (II-2), $x_{31} = x_1 - x_3$, $x_{32} = x_2 - x_3$, etc.

The separation of the motion of the center of mass has reduced the problem from a nine-dimensional to a six-dimensional one. A more useful set of coordinates than the six Cartesian coordinates in Eq. (II-4) can be obtained by defining three variables specifying the triangle formed by the three particles, and three Eulerian angles describing the orientation in space of the plane of the triangle. The most natural choice for the first three coordinates is the interparticle distances, r_{12}, r_{23}, and r_{31}, or any suitable combination of them. The variables employed here are

$$s = r_{31} + r_{23},$$

$$t = r_{31} - r_{23},$$

$$u = r_{12}. \qquad \text{(II-5)}$$

The Eulerian angles are defined as follows: α is the angle between the fixed x axis and the line of nodes (line of intersection between the fixed xy plane and the plane of the particles), and β is the angle between the positive directions of the normals to those two planes. The last angle, γ, is a measure of the rotation of the triangle about its normal. It has been suggested[10] that a possible choice of γ could be made by defining it to be the angle between the line of nodes and one of the principal axes of inertia of the system. While such a choice may be suitable for molecular-like systems it would probably be impractical for atomic systems, and would lead to rather complicated formulas. Instead, γ has been defined to be the angle between the line of nodes and the vector $\underline{r}_{12} = \underline{r}_2 - \underline{r}_1$, where $\underline{r}_1$ and $\underline{r}_2$ are the position vectors of the identical particles in the stationary frame. This choice is meaningful over the entire range of the mass ratio, and also results in a simple behavior of γ under permutation of the identical particles. The transformation of the Hamiltonian into these coordinates, while laborious, is straightforward. The transformation equation and the form of the transformed Hamiltonian are given in terms of the interparticle distances and the Eulerian angles in Appendix I.

It will prove convenient later to have the Hamiltonian expressed in terms of the charge ratio

$$\sigma = Z_3/Z;$$

then the potential V may be written

$$V = Z^2(\sigma/r_{23} + \sigma/r_{31} + 1/r_{12}). \qquad \text{(II-6)}$$

It is also possible to adopt charge-dependent units defined by

$$a_0' = a_0/Z^2,$$

$$\epsilon' = Z^4\epsilon,$$

in which case the potential becomes

$$V' = \sigma/r_{23}' + \sigma/r_{31}' + 1/r_{12}'. \qquad \text{(II-7)}$$

Note that the form of the kinetic energy operator is not affected by this transformation. It follows that the energies obtained with Eq. (II-6) and Eq. (II-7) are related by

$$E = E'/Z^4,$$

and also

$$r_{ij} = Z^2 r_{ij}'. \qquad \text{(II-8)}$$

III. WAVEFUNCTIONS

The angular dependence of the wavefunctions[11] for $L = 1$ is given by the representation coefficients of the irreducible representations of the three-dimensional rotation group, $D^1_{\mu',M_Z}(\alpha,\beta,\gamma)$. The angular momentum $L = 1$ has a space-z-component, M_Z, and a body-z-component, μ'. The radial part was taken in the form of a polynomial in u, s, and t, times a suitable exponential. For atomic systems (very small ρ) excellent results have been obtained with exp[-as + abt] while molecular systems (very large ρ) are described well by a Gaussian $\exp[-c(u - u_0)^2]$.

1. States with $M_Z = 0$

For states with $M_Z = 0$ the three matrix elements, $D^1_{\mu',0}$, are

$$2^{-\frac{1}{2}} \sin\beta e^{-i\gamma},\ \cos\beta,\ -2^{-\frac{1}{2}} \sin\beta e^{+i\gamma}, \qquad \text{(III-1)}$$

for $\mu' = -1, 0, +1$, respectively. It is easily verified[12] that the functions (III-1) are eigenfunctions of L^2 and M_Z, namely

$$L^2 D^1_{\mu',0} = 2\hbar^2 D^1_{\mu',0},$$

$$M_Z D^1_{\mu',0} = 0,$$

for $\mu' = -1, 0, +1$. Any linear combination of the set (III-1), in particular the functions

$$\sin\beta \sin\gamma,\ \sin\beta \cos\gamma,\ \cos\beta, \qquad \text{(III-2)}$$

are also eigenfunctions of L^2 and M_z. The first two members of the set (III-2) are of odd parity while the third one has an even parity as may be seen by inspection from the formulae in Appendix I. It has been shown by Breit[13] that the third term, $\cos\beta$, when used in a wavefunction describing a two electron atomic system corresponds to the case of equivalent orbits and is energetically unsuitable. The remaining two terms, $\sin\beta \sin\gamma$ and $\sin\beta \cos\gamma$, are the angular functions used here. The permutation operator, P_{12}, which permutes the identical particles, when operating on the angular part of the wavefunctions gives

$$P_{12}\sin\beta \sin\gamma = - \sin\beta \sin\gamma,$$

$$P_{12}\sin\beta \cos\gamma = \sin\beta \cos\gamma. \qquad \text{(III-3)}$$

Thus the Eqs. (III-3) serve to determine the permutational symmetry of the radial part of the wavefunctions.

The choice of the form of the radial part depends on the value of the mass ratio ρ. The polynomials must be of such nature as to allow the wavefunctions to pass over into[14]

$$\Phi = F_1(r_1,r_2,r_{12})\cos\theta_1 - F_2(r_1,r_2,r_{12})\cos\theta_2,$$

with

$$F_2(r_1,r_2,r_{12}) = \pm F_1(r_2,r_1,r_{12})$$

as $\rho \to 0$, and into an acceptable molecular wavefunction of Σ-symmetry as $\rho \to \infty$. This can be accomplished by writing

$$\psi = [u^2(f + \tilde{f}) + st(f - \tilde{f})]\sin\beta \sin\gamma$$

$$- 2Q(f - \tilde{f})\sin\beta \cos\gamma, \qquad \text{(III-4a)}$$

where

$$f = P(s,t,u)\exp\tfrac{1}{2}[-as+abt-c(u-u_0)^2], \qquad \text{(III-4b)}$$

$$P(s,t,u) = \sum_{\ell,m,n=0} \lambda_{\ell mn} s^{\ell} t^{m} u^{n-l}, \qquad \text{(III-4c)}$$

$$\tilde{f}(t) = \pm f(-t), \qquad \text{(III-4d)}$$

and $\lambda_{\ell mn}$, a, b, c, and u_0 are the variationally determined constants. The symmetry of the limiting cases of ρ is determined by the choice of signs in Eq. (III-4d). With $\tilde{f}(t) = f(-t)$ the wavefunction is antisymmetric under permutation of the identical particles, while with $\tilde{f}(t) = - f(-t)$ it is symmetric. Thus for atomic systems ($\rho \to 0$) the + sign is to be used to describe triplets, the - sign to describe singlets. For molecular systems it is only necessary to establish the behavior of the wavefunction with respect to a change in sign of the electronic coordinates. Such an operation, however, is equivalent to an inversion at the center of symmetry followed by a permutation of the identical particles. Since the angular functions have negative parity the + sign

(antisymmetric) gives rise to $^2\Sigma_g$ states while the - sign (symmetric) yields $^2\Sigma_u$ states. The conventional atomic and molecular symmetry classifications, however, are based on the assumption of infinite nuclear masses. To avoid confusion the various states have been classified here by their permutational symmetry, i.e. they have been designated as either symmetric or antisymmetric.

2. States with $M_Z = \pm 1$

For states with $M_Z = \pm 1$ the matrix elements, $D^1_{\mu',\pm 1}$, are

$$e^{\pm i\alpha}(1 \mp \cos\beta)e^{-i\gamma}/2,$$

$$\pm e^{\pm i\alpha}\sin\beta/\sqrt{2},$$

$$e^{\pm i\alpha}(1 \pm \cos\beta)e^{i\gamma}/2, \qquad \text{(III-5)}$$

for $\mu' = -1, 0, +1$, respectively. An analysis similar to the one which led to the wavefunction (III-4) now shows that for $M_Z = \pm 1$ a correct wavefunction should be of the form

$$\psi_{\pm 1} = \Big\{[2Q(\cos\beta\,\cos\gamma \pm i\,\sin\gamma) + st(\cos\beta\,\sin\gamma \pm i\,\cos\gamma)] \times (f + \tilde{f}) + u^2(\cos\beta\,\sin\gamma \pm i\,\cos\gamma)(f - \tilde{f})\Big\} e^{\mp i\alpha} \qquad \text{(III-6)}$$

where all the symbols have the same meaning as before. The functions ψ_{+1} and ψ_{-1} are degenerate for both the atomic and molecular systems. The real part of $\psi_{\pm 1}$, e.g., may be written

$$\mathrm{Re}[\psi_{+1}] \equiv \psi = -[u^2(f-\tilde{f}) + st(f+\tilde{f})](\cos\alpha\cos\gamma - \sin\alpha\cos\beta\sin\gamma)$$

$$+ 2Q(f+\tilde{f})(\cos\alpha\sin\gamma + \sin\alpha\cos\beta\cos\gamma), \qquad \text{(III-7)}$$

and the imaginary part as

$$\pm\,\mathrm{Im}[\psi_{\pm}] = -[u^2(f-\tilde{f}) + st(f+\tilde{f})](\sin\alpha\cos\gamma + \cos\alpha\cos\beta\sin\gamma)$$

$$+ 2Q(f+\tilde{f})(\sin\alpha\sin\gamma - \cos\alpha\cos\beta\cos\gamma). \qquad \text{(III-8)}$$

Again, the angular functions in Eq. (III-7) have odd parity, while their behavior under permutation of the identical particles is given by

$$P_{12}(\cos\alpha\cos\gamma - \sin\alpha\cos\beta\sin\gamma) = -(\cos\alpha\cos\gamma - \sin\alpha\cos\beta\sin\gamma),$$

$$P_{12}(\cos\alpha\sin\gamma + \sin\alpha\cos\beta\cos\gamma) = \cos\alpha\sin\gamma + \sin\alpha\cos\beta\cos\gamma.$$

Consequently, when $\tilde{f}(t) = f(-t)$, the wavefunction (III-7) is symmetric, while for $\tilde{f}(t) = -f(-t)$ it is antisymmetric under permutation of the identical particles. In this note only the states with $M_z = 0$ (Σ states) are considered in detail.

IV. RESULTS

It is convenient to divide all the investigated systems into three groups. The systems of the first group are characterized by the charge ratio, $\sigma = Z_3/Z = -1$. The two lowest roots of the secular equation together with the nonlinear parameters and the expectation

values for various r_{ij}^n for these systems are shown in Table I in order of decreasing mass ratio ρ. The only stable systems for $\sigma = -1$ are of the antisymmetric type, and consequently the symmetric states have not been considered. The systems of the second group are characterized by $\sigma = -2$. Here both the symmetric as well as the antisymmetric states are stable. As it happens, there are very few real systems in this category, and most of the tabular entries are simply points needed for the graphs. Table II contains the two lowest roots, nonlinear parameters and expectation values $\langle r_{ij}^n \rangle$ for the antisymmetric states, while the corresponding results for the symmetric states are shown in Table III. Finally, in the third group is the He isoelectronic sequence. The energies, parameters, and the calculated as well as the experimental values of the isotope shifts for He and Li^+ are reported in Table IV for both antisymmetric (2^3P) states and the symmetric (2^1P) states. Calculations have been completed for the Helium isoelectronic sequence through Ne^{+8}, and will form the content of a separate report.[15]

The values of the masses on which the results are based are the subject of Appendix III.

V. DISCUSSION

1. General Remarks

In general, the existence of multiple minima is to be expected with expansions of the size employed here. Although large initial spacings have been used to minimize the possibility of overlooking a true

minimum, no assurance can be given that this has not happened occasionally. Numerical interpolation together with graphical methods has been used to optimize the nonlinear parameters. In view of the fact that the main emphasis of this investigation lies in the broad aspects of the three particle system with an arbitrary mass ratio, substantially the same terms have been used in Eq. (III-4c) for the description of all the systems. The terms have been chosen in the order of increasing metric, i.e. the polynomial in a 10-term wavefunction includes all the possible terms through second degree in u, s, and t; a 20-term wavefunction includes all terms through third degree in u, s, and t, etc.

In terms of the conventional classification of atomic and molecular systems the energies reported here for the molecular systems are to be regarded as the first rotational levels[16] (of the zero and first vibrational levels) of the Σ_g and Σ_u states. In the atomic systems the total angular momentum of unity is the resultant of the angular momenta of the 1s and 2p electrons. For all but the extreme values of the mass ratio, however, it can only be said with justification that the systems possess a total angular momentum of unity with no reference to the manner in which this angular momentum is distributed. C. A. Coulson (private communication) has suggested that all of the states considered here be referred to as P states regardless of their molecular or atomic character, since the total angular momentum as well as its z-component have been quantized.

The energies of molecular systems with infinite molecular masses (labeled $\rho = \infty$ in the tables) are based on the value of the mass ratio $\rho = 10^8$ (10^4 in one case). This value of ρ is more consistent with the formulation of the problem since for truly infinite nuclear masses the variables u, β, and γ become constants. To the accuracy reported, these results, of course, should be identical to those with $\rho = \infty$. Also, the values of the parameter c for these systems ($\rho = \infty$) have not been fully optimized, but were chosen reasonably large, yet small enough so as not to lead to arithmetic difficulties. The parameter c is analogous to a force constant, and consequently can be expected to increase without limit as ρ becomes infinitely large.

The wavefunction (III-4) with $c \neq 0$ has the disadvantage that for very large values of the mass ratio the basis set is linearly dependent. In this range of ρ, the u_0 and $\langle u \rangle$ are essentially equal while c is large. As a result, the wavefunction behaves somewhat like a δ function, and the overlap matrix becomes nearly singular, i.e. one or more of its eigenvalues become very small or vanish. Consequently, the expansions must be limited to a relatively small number of terms. The ratio of the largest and smallest eigenvalues of the overlap matrix has been used as a criterion for the numerical instability in a given case. In addition the optimized energies have been recomputed with the terms rearranged and the extent of agreement noted. In this manner the number of terms used and the number of significant figures reported in the

tables has been determined. For $H_2^+(\infty)$ the ratio of the largest and smallest eigenvalue of the overlap matrix was found to be 1.11×10^6 for the energy reported in Table I. As the mass ratio decreases the linear dependency problem becomes progressively less critical. Thus for the system pμp this ratio was 3.65×10^7 for a wavefunction with four times as many terms as that for $H_2^+(\infty)$. It is interesting to note that for $H_2^+(\infty)$ only 10 terms with $c \neq 0$ were sufficient to yield $E_0 = -.6025036$ a.u. which agrees to two parts in ten thousand with the exact value (Hylleraas[17] obtained $E_{exact} = -.60264...$ a.u.) while a 40-term calculation with $c = 0$ gave only $E_0 = -.581948$ a.u. On the other hand a similar comparison in the case of pμp revealed that a 40-term wavefunction with c included improved the energy only in the fifth significant figure over a 50-term wavefunction with $c = 0$. The foregoing arguments indicate that the linear dependency of the basis set $c \neq 0$ is less of a drawback than it may appear to be. The convergence of this set as a function of the mass ratio is such as to allow the set to describe the systems reasonably well regardless of the severity of the linear dependency.

The results reported here were obtained by means of programs written for the CDC 1604 electronic computer located in the Computation Center of The University of Texas. The secular equations were solved by the Schmidt-Jacobi rotation method. For a 50-term wavefunction the average running time was slightly over 20 minutes per set of parameters,

for a 10-term wavefunction it was under 5 minutes per similar set. The necessary integrals and methods of evaluating them are discussed in Appendix II.

2. Charge Ratio $\sigma = -1$

This group includes the molecules H_2^+, D_2^+, and T_2^+, and the mesonic systems $p\mu p$, $d\mu d$, and $t\mu t$. The lowest root, E_0, is plotted against log ρ in Fig. 1. The ground state ($L = 0$) energies, where known, are also plotted for comparison on the same graph. The expectation values of various r_{ij}^n are shown in Fig. 2. In the infinite mass limit, and to a good approximation also for the large values of ρ(i.e. the systems, T_2^+, D_2^+, and H_2^+), the parameter u_0 should represent the equilibrium internuclear distance and hence be equal to $\langle u \rangle$. As the mass ratio becomes smaller, u_0 approximates the average internuclear distance evermore poorly due to the anharmonicity of the vibrations. When the masses become nearly equal such an interpretation loses its meaning altogether. At the same time E_0 lies progressively higher above the ground state energy and, in fact, the results indicate that systems with ρ less than about 4.3 do not exist in a bound state with angular momentum equal to unity although they may be bound in their ground state. This situation is reflected in the fact that the expectation values of r_{ij} and r_{ij}^2 increase sharply while the expectation values of r_{ij}^{-1} tend to zero as ρ approaches 4.3 from larger values.[18]

Very little has been done so far on this problem even by the Born-Oppenheimer or similar approximations to allow for an illuminating comparison of results. Direct variational methods similar to the one employed here have been used to compute only the L = 0 state energies of some of the systems considered in this note. The adiabatic approximation has been used by Cohen et al[19] to calculate the L = 1 states of the mesonic molecules pμp, dμd, and tμt. Unfortunately, both of these papers lack a clear statement concerning the values of the masses and conversion factors employed in calculating the reported energies. Cohen et al obtained the total energies -2623 ev and -2887 ev for the system pμp and dμd, respectively. Belyaev reported the binding energies for pμp, dμd, and tμt to be 109 ev, 226 ev, and 288 ev, respectively. Since in reduced atomic units the two particle energy is -0.5 for all systems, the values of E_0 shown in Table I lead to the binding energies for the mesonic molecules of 106.8 ev, 226.3 ev, and 288.8 ev, while the total energies are -2635.0 ev, -2889.2 ev, and -2999.7ev.

3. Charge Ratio σ = - 2

In contrast to the σ = - 1 case, binding is found here for the symmetric as well as the antisymmetric states over the entire range of values of the mass ratio. Consequently, "atomic" wavefunctions (c = 0 in III-4) have been used for small values of ρ($\rho < \sim 10$) while "molecular" wavefunctions (b = 0 in III-4) have been employed for large values of

$p(\rho > \sim 1)$. The intermediate region has been computed with both types of wavefunctions for comparison. The energies obtained with the atomic wavefunction are better in both the symmetric and antisymmetric states through ρ values of about 10.

Figs. 3-6 show the energies and expectation values as function of log ρ. The striking feature is the clear division of the systems into two groups with predominantly either atomic or molecular character. While more pronounced in the antisymmetric states, this phenomenon is present in both of the symmetry groups. It should be noted that at the atomic end the energy curve for the antisymmetric states (triplets) starts to drop from the very beginning, i.e. at He($\rho = 0$), while the corresponding curve for the symmetric states (singlets) first rises slightly towards the more positive energy values before falling off towards the lower values in the molecular region. This behavior is to be expected and is consistent with the fact that the mass-polarization effect lowers the energy in triplets while raising it in singlets.

Arithmetic considerations made it necessary to use $\rho = 10^4$ in the "infinite" mass calculation of the symmetric (Σ_u) state. It is quite evident, however, that both the Σ_g and Σ_u energies approach the exact infinite mass values[21] of -3.808 a.u. and -2.309 a.u., respectively. The negative values of the parameter u_0 in the $\rho = 1$ and $\rho = 10$ antisymmetric states indicate that the Gaussian exponential is not very suitable for systems with only moderately large values of the mass ratio. Moreover, if u_0 assumes large negative value while c is very small as in the $\rho = 1$ antisymmetric case, then

$$- c(u - u_0)^2 \approx - 2cu_0u + \text{const}, \quad u_0 \ll 0, \quad c \ll 1.$$

This indicates that a better description of this system would be obtained with an exponential linear in u. In order to indicate that better descriptions are possible in this region, the corresponding portions of the curves on the graphs have been drawn dashed. Except for the systems $\rho = 0$ (which is discussed in Section VI) and $\rho = \infty$ there has been no previous work done on any of the systems in this category.

VI. THE HELIUM ISOELECTRONIC SYSTEM

A. Isotope Shifts

The material in this subsection has already appeared elsewhere in a preliminary form[22]. The numerical results presented here constitute a slight improvement over the earlier report.

In 1930 Hughes and Eckart[23] employed center-of-mass coordinates to achieve the separation of the translational motion of the center of mass and the internal motion of a system of three particles. Assuming a simple open shell hydrogen-like wavefunction, they have, by perturbation theory, obtained an analytical expression for the mass effect of a two-electron atom. When experimental methods became sufficiently refined to allow accurate measurements to be made on the isotope shift in helium, it was found that the values of the isotope shift calculated from Hughes

and Eckart's formula were in quantitative disagreement with the experimental results.[24,25] The discrepancy was especially pronounced in P states. Except for possibly a few unsuccessful attempts,[26] there has been no further theoretical work done along these lines for excited states, mainly due to the lack of sufficiently accurately wavefunctions. Bethe and Salpeter have stated that "the cause of these discrepancies is not yet known,"[27] while others[24] have suspected the theory itself.

The total mass effect is usually thought of as consisting of two separate parts: the elementary mass correction in energy due to the motion of the nucleus itself, and a much smaller correction arising from the mass polarization (specific shift). The elementary correction affects all the levels of an atom in the same way, is independent of the state of ionization of the atom, and can be computed directly. The second part of the mass correction differs for the various states of the atom. Treated as a perturbation it is proportional to the expectation value of the operator $\nabla_1 \cdot \nabla_2$. It is this second part whose theoretical value was until now responsible for the disagreement with available experimental results for the isotope shift.

The method employed in this work lends itself quite naturally to this type of problem. The Hamiltonian (II-4) as a function of the mass ratio ρ reflects the entire dependence of the energy on the masses. The connection with experiment is made through the difference of the spectroscopic term values for two isotopes of the same atom. The spectroscopic term value is the total (two-electron) atomic energy less the

corresponding hydrogen-like (one-electron) energy, $-\frac{1}{2}Z^2$. The results are shown in Table IV.

The discrepancy between the theoretical and experimental values for the isotope shift in He has now been brought within the limits of experimental accuracy. On the basis of the agreement for helium, it can probably be said with some confidence that the calculated results for Li^+ are accurate to within 1%.

B. Energies for $\rho = 0$; Comparison with Pekeris, Schiff, and Lipson[28]

The energies computed for the 2^1P and 2^3P states of the helium atom with $\rho = 0$ are compared in Table V with the results of Pekeris et al for the same systems. The 50-term values reported here are slightly better than the 220-term values that they obtained, though, as is to be anticipated, they lie above their extrapolated estimates of the true energies. The superiority of the 50-term results, of course, resides in the fact that the wavefunction (III-4) contains two nonlinear parameters, each of which has been fully optimized, whereas Pekeris et al preselected their corresponding nonlinear parameters. It is, however, interesting to see just how well their preselected parameters function when used in a 50-term wavefunction. These parameters are

$$2^1P: \alpha = 2.4977, \beta = 0.601;$$

$$2^3P: \alpha = 2.5161, \beta =$$

The corresponding energies are entered in Table V.

APPENDIX I. THE COORDINATE TRANSFORMATION

The three vectors forming the sides of the triangle of the particles are defined in terms of the position vectors of the particles, i.e.

$$\underset{\sim}{r}_{ij} = \underset{\sim}{r}_j - \underset{\sim}{r}_i,$$

and hence

$$r_{ij} = \left[(x_j - x_i)^2 + (y_j - y_i)^2 + (z_j - z_i)^2\right]^{\frac{1}{2}},$$

where x_k, y_k, z_k are the Cartesian coordinates of the particles in the fixed frame. Note that $x_{ij} = - x_{ji}$, etc. The Eulerian angles are then defined by means of the vectors $\underset{\sim}{r}_{ij}$ as follows. Let $\underset{\sim}{i}$ and $\underset{\sim}{k}$ be unit vectors in the positive x and z directions, respectively, $\underset{\sim}{k}'$ a unit vector in the positive z' direction, and $\underset{\sim}{n}$ a unit vector along the line of nodes such that

$$\underset{\sim}{k}' = \frac{\underset{\sim}{r}_{23} \times \underset{\sim}{r}_{31}}{|\underset{\sim}{r}_{23} \times \underset{\sim}{r}_{31}|}, \qquad \underset{\sim}{n} = \frac{\underset{\sim}{k} \times \underset{\sim}{k}'}{|\underset{\sim}{k} \times \underset{\sim}{k}'|}.$$

Then

$$\cos\alpha = \underset{\sim}{i} \cdot \underset{\sim}{n},$$

$$\cos\beta = \underset{\sim}{k} \cdot \underset{\sim}{k}',$$

$$\cos\gamma = (\underset{\sim}{n} \cdot \underset{\sim}{r}_{12})/r_{12}.$$

The formulae actually used in the coordinate transformation and which follow from the above definitions of the Eulerian angles are

$$\sin\alpha \sin\beta = (y_{23}z_{31} - z_{23}y_{31})/Q,$$

$$\cos\alpha \sin\beta = (x_{23}z_{31} - z_{23}x_{31})/Q,$$

$$\cos\beta = (x_{23}y_{31} - y_{23}x_{31})/Q,$$

$$\sin\beta \sin\gamma = (z_{23} + z_{31})/r_{12},$$

$$\sin\beta \cos\gamma = \left[z_{23}(r_{12}^2 + r_{31}^2 - r_{23}^2) - z_{31}(r_{12}^2 + r_{23}^2 - r_{31}^2)\right]/2r_{12}Q,$$

where Q has been already defined as

$$Q = \left| \underset{\sim}{r}_{23} \times \underset{\sim}{r}_{31} \right|.$$

The Hamiltonian may now be written in terms of the interparticle distances and the Eulerian angles. The transformation, while laborious, is straightforward. The Hamiltonian, after considerable reduction, becomes

$$H = -\tfrac{1}{2}(\rho+1)\Big[(\rho+1)(\partial_{23}^2+\partial_{31}^2)+\rho\cos\Theta_3\,\partial_{23}\partial_{31}$$

$$+\cos\Theta_2\,\partial_{12}\partial_{23}+\cos\Theta_1\,\partial_{31}\partial_{12}+2\partial_{12}^2$$

$$+2(\rho+1)(\Pi_{23}^{-1}\partial_{23}+\Pi_{31}^{-1}\partial_{31})+4\Pi_{12}^{-1}\partial_{12}+(2Q/\Pi_{12}^2\Pi_{23})\partial_{23}\partial_\gamma$$

$$-(2Q/\Pi_{12}^2\Pi_{31})\partial_{31}\partial_\gamma+Q^{-2}\sin^2\beta(\Pi_{31}^2+\Pi_{23}^2+\rho\Pi_{12}^2-A)\partial^2\cos\beta$$

$$+(2\Pi_{12}^{-2}+Q^{-2}\cot^2\beta A)\partial^2\gamma+B(\cos\beta\,\partial\cos\beta\,\partial\gamma+$$

$$\partial\cos\beta\,\partial\alpha+\cos\beta\sin^{-2}\beta\,\partial\alpha)-Q^{-2}\cos\beta(\Pi_{31}^2+\Pi_{23}^2+\rho\Pi_{12}^2)\partial\cos\beta$$

$$+C\sin\gamma\cos\gamma\sin^{-2}\beta\,\partial\gamma+AQ^{-2}\sin^{-2}\beta(\partial^2\alpha+2\cos\beta\,\partial\alpha\,\partial\gamma)\Big]$$

$$+Z^2\Pi_{12}^{-1}+ZZ_3(\Pi_{23}^{-1}+\Pi_{31}^{-1}),$$

where

$$2\Pi_{12}^2A=(2\rho+1)\Pi_{12}^4\sin^2\gamma+\left[2Q\cos\gamma+(\Pi_{23}^2-\Pi_{31}^2)\sin\gamma\right]^2,$$

$$\tfrac{1}{2}\Pi_{12}^2Q^2B=\left[\Pi_{12}^2(\Pi_{23}^2+\Pi_{31}^2+\rho\Pi_{12}^2)-4Q^2\right]\sin\gamma\cos\gamma$$

$$+(\Pi_{23}^2-\Pi_{31}^2)Q(\cos^2\gamma-\sin^2\gamma),$$

$$\Pi_{12}^2Q^2C=2(\Pi_{23}^2-\Pi_{31}^2)Q(\cos^2\beta\cos^2\gamma-\sin^2\gamma)\sin\gamma\cos\gamma-2Q^2(1+2\cos^2\beta)$$

$$+\tfrac{1}{2}\left[\Pi_{12}^4+(\Pi_{23}^2-\Pi_{31}^2)^2\right]+\Pi_{12}^2\cos^2\beta(\Pi_{31}^2+\Pi_{23}^2)+\rho\Pi_{12}^4(1+\cos^2\beta),$$

$$\cos \Theta_i = (r_{ij}^2 + r_{ki}^2 - r_{jk}^2) / r_{ij}\, r_{ki} \quad ,$$

$$Q = \left| r_{23} \times r_{31} \right| ,$$

$$Z = Z_1 = Z_2 ,$$

and $Z_i e$ is the charge of the ith particle. The change from the radial variables r_{ij} to u, s, and t defined in Eq. (II-5) is trivial, and is not considered here.

APPENDIX II. THE INTEGRATIONS

There are two basic types of integrals to be considered. For systems with atomic character the wavefunction (III-4) with c = 0 leads to integrals

$$I(L,N,M) = 1/A! \int_0^\infty ds \int_0^s du \int_0^u dt\, s^L t^M u^N e^{-s} e^{xt}, \qquad \text{(AII-1)}$$

where

$$A = L + M + N.$$

These integrals are essentially the same as those derived by James and Coolidge,[29] and are listed here merely for the sake of completeness.

$$I(0,0,M) = (1 - x)^{-(M + 1)} \qquad \text{(AII-2)}$$

$$I(0,N,0) = [I(0,N - 1,0) + 1]/(1 - x) \qquad \text{(AII-3)}$$

$$I(L,0,0) = [I(L - 1,0,0) + L + 1]/(1 - x) \qquad \text{(AII-4)}$$

$$I(0,N,M) = [MI(0,N,M - 1) + NI(0,N - 1,M)]/A(1 - x) \qquad \text{(AII-5)}$$

$$I(L,0,M) = [LI(L - 1,0,M) + MI(L,0,M - 1)]/A(1 - x) \qquad \text{(AII-6)}$$

$$I(L,N,0) = [LI(L - 1,N,0) + NI(L,N - 1,0) + A(A + 1)/(N + 1)]/A(1 - x) \qquad \text{(AII-7)}$$

$$I(L,N,M) = [LI(L - 1,N,M) + NI(L,N - 1,M) + MI(L,N,M - 1)]/A(1 - x) \qquad \text{(AII-8)}$$

For negative values of N two additional auxiliary functions are needed

$$A(L;y) = \int_0^\infty s^L e^{-ys} ds, \qquad \text{(AII-9)}$$

$$V(L,M) = \int_0^\infty ds \int_0^s dt\ s^L t^M e^{-s} e^{xt}. \qquad \text{(AII-10)}$$

The necessary recursion relations are

$$A(0;y) = 1/y \qquad \text{(AII-11)}$$

$$A(L;y) = LA(L - 1;y)/y \qquad \text{(AII-12)}$$

$$V(-1,0) = - 1/x\ell n(1 - x) \qquad \text{(AII-13)}$$

$$V(-1,M) = - 1/x[MV(-1,M - 1) - A(M - 1;1 - x)] \qquad \text{(AII-14)}$$

$$V(0,M) = A(M;1 - x) \qquad \text{(AII-15)}$$

$$V(L,0) = 1/x[A(L;1 - x) - A(L;1)] \qquad \text{(AII-16)}$$

$$V(L,M) = [LV(L - 1) + MV(M - 1)]/(1 - x). \qquad \text{(AII-17)}$$

Then if

$$I(L,N,M) = 1/A!I'(L,N,M),$$

$$I'(0,-1,M) = V(-1,M) \tag{AII-18}$$

$$I'(L,-1,0) = LI'(L-1,-1,0) + V(L-1,0) \tag{AII-19}$$

$$I'(L,-1,M) = [LI'(L-1,-1,M) + MI'(L,-1,M-1) + V(L-1,M) - V(L,M-1)]/(1-x). \tag{AII-20}$$

Eq. (AII-8) may now be used to further lower N.

When b = 0 in the wavefunction (III-4) the resulting integrals are of the form

$$\int_0^\infty du \int_u^\infty ds \int_{-u}^{u} dt\; s^L t^M u^N e^{-as-c(u-u_0)^2}. \tag{AII-21}$$

The integration over s and t can be performed immediately and for even values of M results in

$$\int_0^\infty du \int_u^\infty ds \int_{-u}^{u} dt\; s^L t^M u^N e^{-as-c(u-u_0)^2}$$

$$= 2/(M+1)a^{(L+1)} \int_0^\infty du\; u^{M+N+1}[(au)^L + L(au)^{L-1}$$

$$+ \ldots + L!(au) + L!]e^{-au-c(u-u_0)^2}. \tag{AII-22}$$

Thus the integral to be evaluated is

$$\int_0^\infty du\ u^p e^{-au-c(u-u_0)^2}$$

$$= e^{-a(u_0-a/4c)}(a/c)^{(p+1)/2}\int_{-\kappa}^{\infty}(x+\kappa)^p e^{-ax^2}dx, \quad \text{(AII-23)}$$

where

$$\kappa = \sqrt{c/a}\,u_0 - 1/2\sqrt{a/c}.$$

The term $\exp[-a(u_0 - a/4c)]$ may be factored out of all the matrix elements; define

$$J(p) = (a/c)^{(p+1)/2}\int_{-\kappa}^{\infty}(x+\kappa)^p e^{-ax^2}dx. \quad \text{(AII-24)}$$

The lowest two integrals are given by

$$J(0) = 1/2\sqrt{\pi/c}[\mathrm{erf}(\infty) + \mathrm{erf}(\kappa\sqrt{a})], \quad \text{(AII-25)}$$

$$J(1) = e^{-a\kappa^2}/2c + \sqrt{a/c}\,\kappa J(0). \quad \text{(AII-26)}$$

All higher integrals may then be obtained by the use of the following recursion formula

$$J(p) = \sqrt{a/c}\,\kappa J(p-1) + (p-1)/2cJ(p-2). \quad \text{(AII-2)}$$

The error function in Eq. (AII-25) was evaluated by means of either the normal or the asymptotic series depending on the value of the argument.

For negative values of the argument the first term on the right in the recursion Eq. (AII-27) becomes negative, and the method rapidly becomes useless due to the loss of accuracy. In such cases it was necessary to resort to numerical integration of the integrals $J(p)$ for two high values of p(64 and 65), and then to use Eq. (AII-27) to recur down. A careful investigation has shown Simpson's rule to be quite satisfactory for that purpose.

APPENDIX III.

Frequently it becomes desirable to express the energies and other physical properties in units other than those in which they are reported. There are two types of atomic units that are being used in the literature. The reduced atomic units are based on the reduced mass of a system of particles while another kind of atomic units is based on the mass of one of the particles in the system. If this particle is an electron these units then become the usual atomic units where the unit of length is the Bohr radius (0.529172 Å); if the particle is a meson the units could be called mesonic atomic units. It is unfortunate that it has become customary to call any and all of these types of units simply atomic units (a.u.). Throughout the text the notation a.u. represents the reduced atomic units. Note that for infinite masses the

reduced atomic units and the Bohr atomic units are identical. For a comparison of various results to be possible a table of the masses on which the calculations are based is necessary. Such is the purpose of Table VI. All the results in Tables I - V are in the reduced atomic units defined in Section II; to convert them into the Bohr atomic units the energies must be multiplied and linear distances divided by the factor μ/m_e whose values for several systems of special interest are shown in Table VII. The results for the mesonic systems can also be expressed in the mesonic atomic units by multiplying the energies by a factor μ/m_μ and distances by its reciprocal.[30]

The results of Tables II and III, while being specifically for systems with $Z = -1$ and $Z_3 = 2$, may easily be made to apply to systems with any value of Z and Z_3 such that their ratio $\sigma = Z_3/Z = -2$. As has been mentioned in Section II it is possible to work in charge-dependent units in which case the Eqs. (II-8) may be used to convert the results for one system with a given set of charges to those for a different one. Thus, for example, by dividing the energy of the system $\rho = 10^8$ in Table II by 16 one obtains the energy of the system with the same mass ratio, but where the nuclei each have one half of the charge of a proton, and the odd particle has the electronic charge. The energies reported in ev are based on the value

$$m_e e^4 \hbar^{-2} = 27.2097 \text{ ev.}$$

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30. Note the two different meanings of the symbol μ.

TABLE I

ENERGIES, PARAMETERS, AND EXPECTATION VALUES[a] FOR ANTISYMMETRIC STATES, $\sigma = -1$.

System	ρ	$-E_0$	$-E_1$	a	c	u_0	$\langle u \rangle$	$\langle u^{-1} \rangle$	$\langle u^2 \rangle$	$\langle r_{31} \rangle$	$\langle r_{31}^2 \rangle$	$\langle r_{31}^{-1} \rangle$	N[b]
	∞[b]	.6025036	.5889	1.36	576.0	1.995	1.997	.5010	3.987	1.657	3.387	.8530	10
T_2^+	5496.93	.5994830	.59317	1.563	15.6	2.01	2.036	.4949	4.172	1.678	3.485	.8468	20
D_2^+	3670.44	.5987690	.59112	1.563	12.5	2.01	2.044	.4936	4.214	1.682	3.506	.8454	20
H_2^+	1836.12	.5971388	.58655	1.563	8.43	2.01	2.064	.4905	4.314	1.693	3.558	.8424	20
	500	.59189962	.5726575	1.57	3.86	1.99	2.132	.4803	4.648	1.728	3.730	.8320	20
	100	.57766559	.5402124	1.57	1.24	1.91	2.330	.4512	5.684	1.831	4.251	.8033	20
$t\mu t$	26.586	.55227525	.50585276	1.84	0	0	2.804	.3947	8.614	2.072	5.676	.7499	50
		.5532721	.5042056	1.62	0.433	2.24	2.783	.3954	8.273	2.053	5.531	.7510	40
$d\mu d$	17.752	.54202124	.49855109	1.78	0	0	3.030	.3694	10.16	2.188	6.438	.7270	50
		.5424934	.4929453	1.58	0.265	2.21	3.004	.3693	9.908	2.176	6.331	.7271	40
$p\mu p$	8.8805	.52107504	.49095416	1.64	0	0	3.714	.3106	15.721	2.539	9.177	.6754	50
		.5211225	.4810963	1.51	.076	1.58	3.687	.3114	15.403	2.525	9.021	.6770	40

[a] In reduced atomic units.

[b] Actually 10^8, see section V.

[c] Number of terms in the polynomial, Eqn. (III-4c).

TABLE II

ENERGIES, PARAMETERS, AND EXPECTATION VALUES[a] FOR ANTISYMMETRIC STATES, $\sigma = -2$.

System	ρ	$-E_0$	$-E_1$	a	b	c	u_0	$\langle u \rangle$	$\langle u^{-1} \rangle$	$\langle u^2 \rangle$	$\langle r_{31} \rangle$	$\langle r_{31}^2 \rangle$	$\langle r_{31}^{-1} \rangle$	N[c]
	∞[b]	3.807756	3.789586	1.64	0	900.0	.516	.5175	1.934	.2679	.5777	.4161	2.387	10
	500	3.701662	3.525421	1.70	0	8.74	.474	.5663	1.831	.3317	.6027	.4554	2.308	20
	100	3.548500	3.204489	1.75	0	2.76	.367	.6440	1.668	.4420	.6419	.5190	2.192	20
	10	2.959477	2.406181	1.89	0	0.70	-1.63	1.058	1.082	1.257	.8484	.9347	1.750	20
		2.95530		5.0	.032	0	0							40
	1	2.265595	2.041171	2.79	0	0.0001	-2800	2.505	0.4882	7.464	1.570	3.858	1.255	40
		2.2659965	2.0795342	3.12	.086	0	0	2.521	0.4865	7.602	1.579	3.929	1.255	50
$\mu\alpha\mu$	.028345	2.1350992	2.0561019	2.53	.32	0	0	4.615	0.2720	25.74	2.632	12.77	1.136	50
He^4	1.37091×10^{-4}	2.13317237	2.0566775	2.71	.384	0	0	4.6994	0.2667	26.634	2.674	13.21	1.1333	50
He	0	2.13316352	2.0566735	2.71	.308	0	0	4.6998	0.2666	26.638	2.674	13.21	1.1332	50

[a] In reduced atomic units.

[b] Actually 10^8, see Section V.

[c] Number of terms in the polynomial, Eq. (III-4c).

TABLE III

ENERGIES, PARAMETERS, AND EXPECTATION VALUES[a] FOR SYMMETRIC STATES, $\sigma = -2$.

System	ρ	$-E_0$	$-\bar{E}_1$	a	b	c	u_0	$\langle u \rangle$	$\langle u^{-1} \rangle$	$\langle u^2 \rangle$	$\langle r_{31} \rangle$	$\langle r_{31}^2 \rangle$	$\langle r_{31}^{-1} \rangle$	N[c]
	∞[b]	2.303806	2.233081	2.07	0	28.1	2.45	2.472	.4057	6.128	1.644	3.784	1.254	10
	500	2.293306	2.203830	1.04	0	1.50	2.44	2.542	.3984	6.536	1.678	3.983	1.246	20
	100	2.275847	2.150955	1.04	0	0.578	2.41	2.651	.3872	7.206	1.731	4.304	1.235	20
		2.265118	2.178534	2.62	.081	0	0							40
	10	2.207989	1.973948	2.08	0	0.360	2.03	3.124	.3435	10.39	1.956	5.798	1.189	20
		2.2172190	2.1219592	2.46	.101	0	0	3.336	.3266	12.04	2.061	13.26	1.190	40
	1	2.127041	1.993702	2.62	0	0.016	15.5	4.569	.2530	23.53	2.649	12.05	1.127	40
		2.1338256	2.0506895	2.33	.115	0	0	4.976	.2364	28.42	2.854	14.52	1.126	50
$\mu\alpha\mu$	.028345	2.1226943	2.0521393	2.47	.34	0	0	5.199	.2412	32.27	2.943	16.12	1.122	50
He^4	1.37091×10^{-4}	2.12383564	2.0537407	2.75	.4193	0	0	5.138	.2450	31.59	2.911	15.76	1.1232	50
He	0	2.12384195	2.0537433	2.75	.4193	0	0	5.137	.2451	31.58	2.910	15.76	1.1232	50

[a] In reduced atomic units.

[b] Actually 10^4, See Section V.

[c] Number of terms in the polynomial, Eq. (III-4c).

TABLE IV

ATOMIC ENERGIES, PARAMETERS, AND ISOTOPE SHIFTS

System	Rydberg (cm^{-1})	$\rho \times 10^4$	a	b	Energy (a.u.)	Isotope Shift calc. (cm^{-1})	Isotope Shift exp (cm^{-1})
2^1P, He^3	109717.345	1.8196	2.75	.4193	-2.12383358	1.67 (1.58)[a]	1.68±.005[b] 1.67[c]
2^1P, He^4	109722.267	1.3709			-2.12383565		
2^1P, $(Li^+)^6$	109727.295	0.9126	4.36	.2970	-4.99332659	2.13 (2.032)[a]	---
2^1P, $(Li^+)^7$	109728.723	0.7825			-4.99332987		
2^3P, He^3	109717.345	1.8196	2.71	.3840	-2.13317527	0.67 (0.745)[a]	0.675[c]
2^3P, He^4	109722.267	1.3709			-2.13317237		
2^3P, $(Li^+)^6$	109727.295	0.9126	4.45	.3075	-5.02774288	0.63 (p.653)[a]	---
2^3P, $(Li^+)^7$	109728.723	0.7825			-5.02773889		

[a]Calculated from the Hughes-Eckhart formula, footnote 23.

[b]Bradley and Kuhn, loc. cit.

[c]Fred et al, loc. cit.

TABLE V

A COMPARISON WITH PEKERIS, SCHIFF, AND LIPSON:
THE HELIUM ATOM ENERGIES (ATOMIC UNITS) FOR THE CASE $\rho = 0$

State	MS[a]	PSR - 220	PSL - ∞	PSR - 50
2^1P	-2.123841954	-2.12384140	-2.12384267	-2.1238400
2^3P	-2.1331635	-2.13316331	-2.13316413	

Key: MS, This paper; PSL - 220, PSL - ∞ results due to Pekeris et al, footnote 28, from their 220 term wave function and from their extrapolated estimates, respectively; PSL - 50, this paper, using the non-linear parameter values used by Pekeris et al in the construction of their wavefunctions.

TABLE VI

MASSES OF ELEMENTARY PARTICLES[a]

α[b]	t[c]	d[c]	p[c]	u[d]	e
7294.4	5496.93	3670.44	1836.13	206.76	1.0

[a] In units of the electron mass.

[b] Computed from $R_\infty/R_{He}{}^4 = 1 + m_e/m_\alpha = 1.00013709$.

[c] Based on the following values taken from the American Institute of Physics Handbook (McGraw-Hill, New York, 1957):

$m_p/m_e = 1836.13$,

$m_p = 1.007595$ a.m.,

$m_d = 2.014190$ a.m.,

$m_t = 3.01650$ a.m.

[d] G. Shapiro and L. M. Lederman, Phys. Rev. 125, 1022 (1962).

TABLE VII

CONVERSION FACTORS[a]

System	μ/m_e	μ/m_μ
H_2^+ (∞)	1.0	--
T_2^+	0.999818	--
D_2^+	0.999728	--
H_2^+	0.999456	--
$t\mu t$	199.26_5	0.96375
$d\mu d$	195.73_4	0.94667
$p\mu p$	185.83_4	0.89879
$\mu\alpha\mu$	201.06	0.97243

[a]In the column headings μ = reduced mass and m_μ = mass of meson. In the row headings μ indicates a μ-meson.

LEGEND FOR FIGURE 1

The $L = 0$ and $L = 1$ energies in reduced atomic units as function of $\lg\rho$ for systems with the charge ratio $\sigma = -1$. The $L = 0$ results are taken from references 1-6.

LEGEND FOR FIGURE 2

The expectation values of r_{ij}^{n} in reduced atomic units as function of $\lg \rho$ for systems with the charge ratio $\sigma = -1$.

LEGEND FOR FIGURE 3

Charge ratio $\sigma = -2$. The $L = 1$ energies in reduced atomic units of the symmetric and antisymmetric states as function of $\lg \rho$. The shape of the curves near $\rho = 1$ is not definitely established from the information given in Tables 2 and 3, and consequently the curves in this region are shown dotted.

LEGEND FOR FIGURE 4

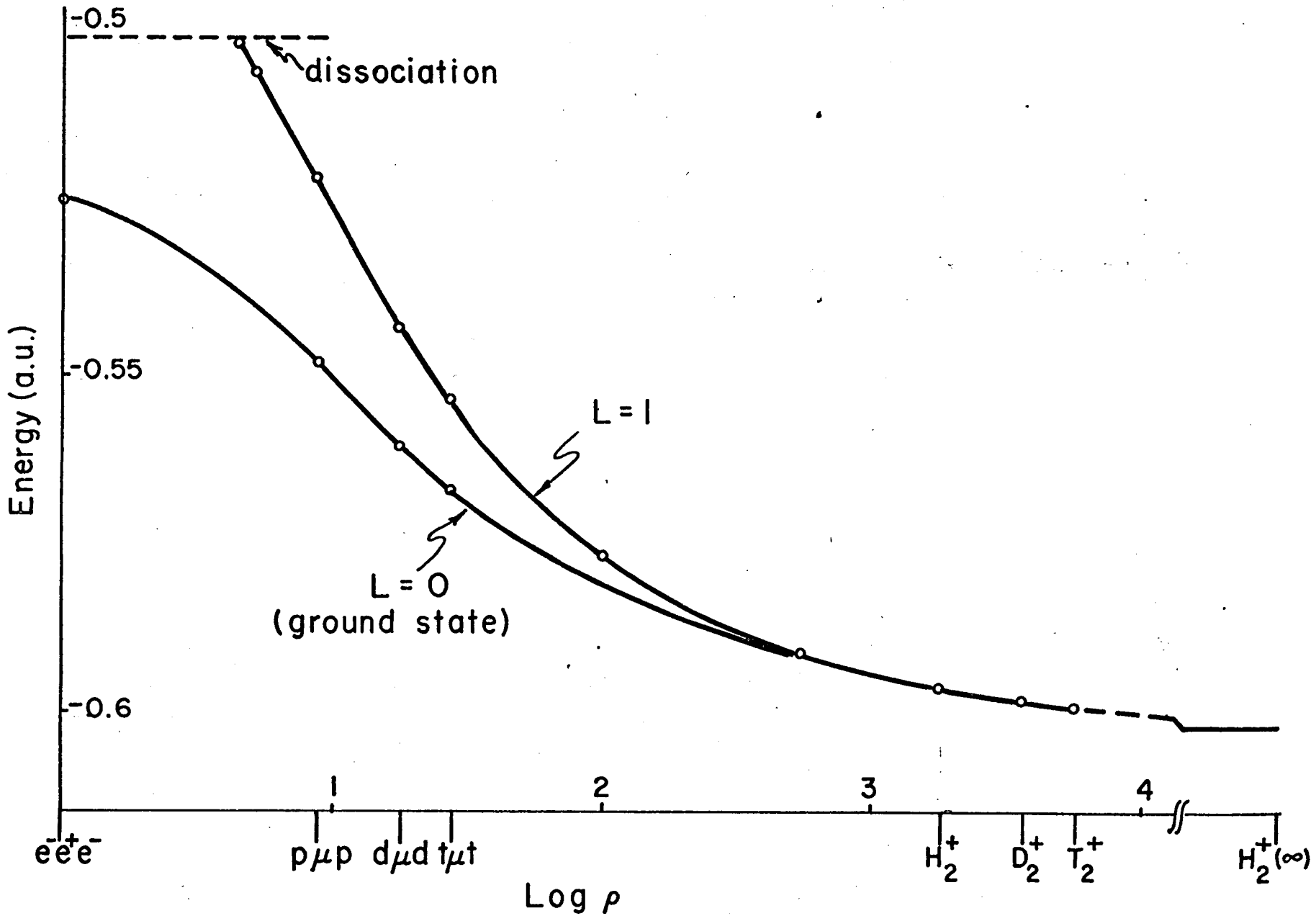
Charge ratio $\sigma = -2$. The expectation values of r_{ij}^{-1} in reduced atomic units for the symmetric and antisymmetric states as a function of $\lg \rho$. The shape of the curves near $\rho = 1$ is not definitely established from the information given in Tables 2 and 3, and consequently the curves in this region are shown dotted. Where the scale of the graphs permits, the values for $\rho = 1$ obtained with the atomic and molecular wavefunctions are shown separately.

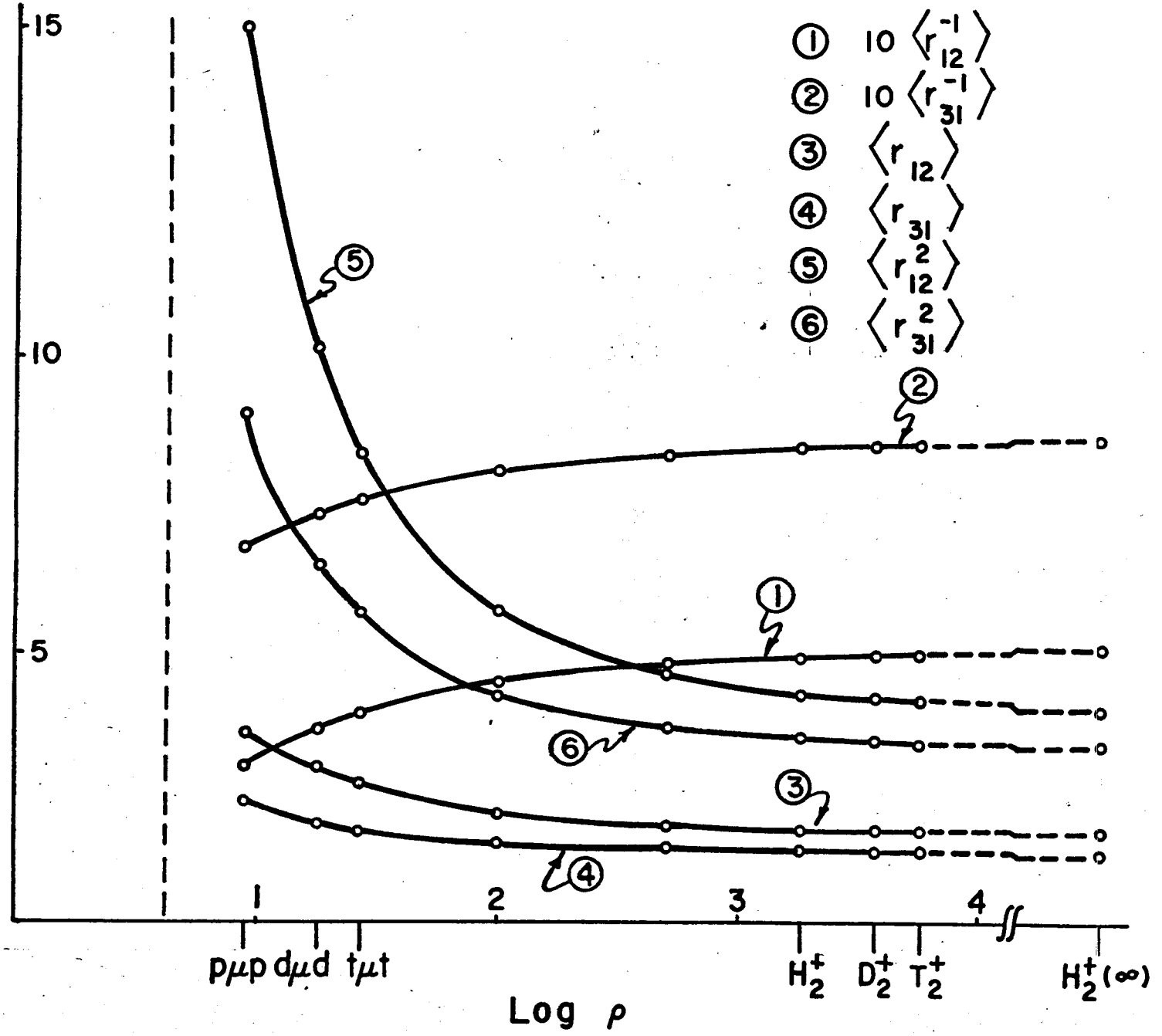
LEGEND FOR FIGURE 5

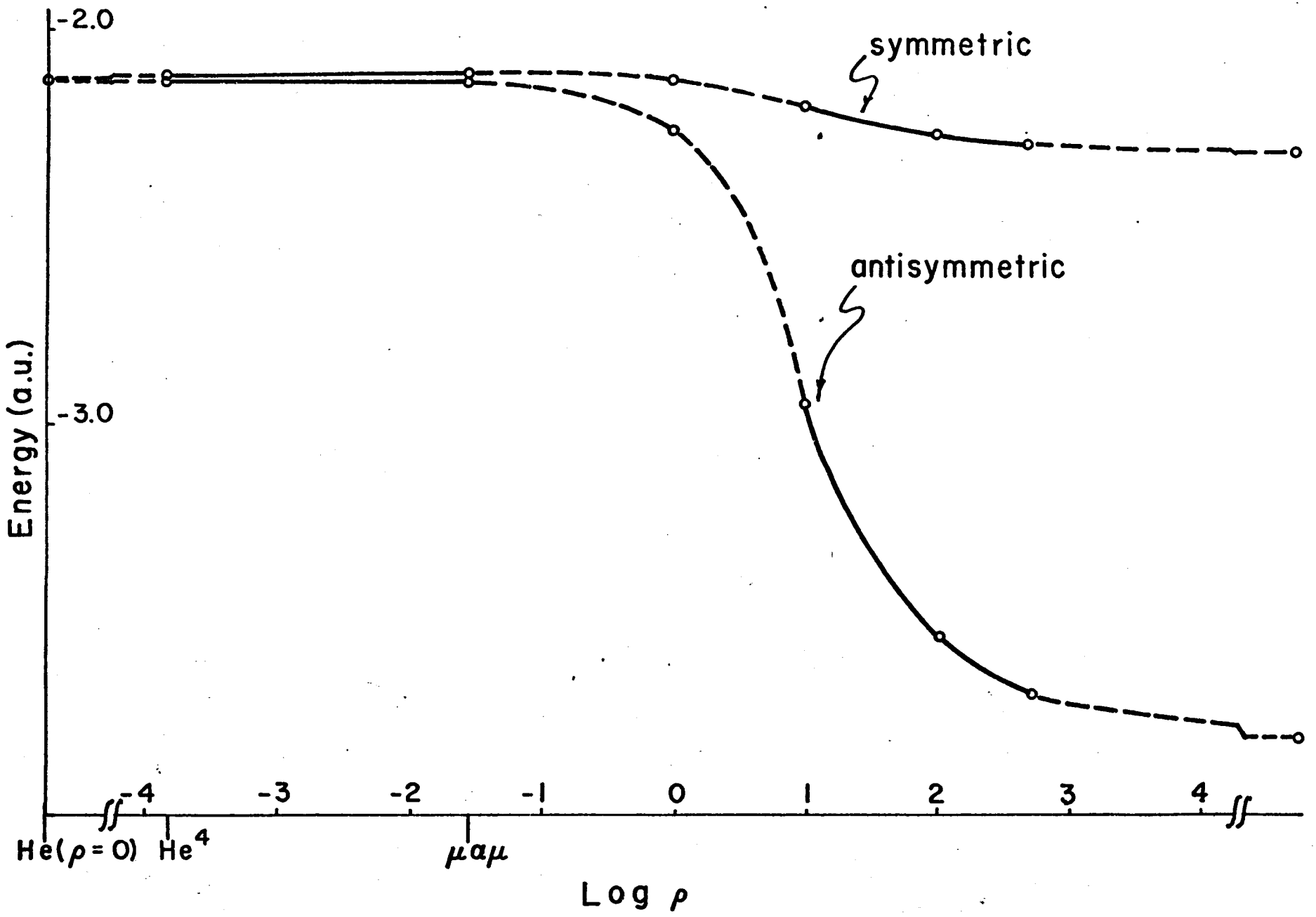
Charge ratio $\sigma = -2$. The expectation values of r_{ij} in reduced atomic units for the symmetric and antisymmetric states as a function of $\lg \rho$. The shape of the curves near $\rho = 1$ is not definitely established from the information given in Tables 2 and 3, and consequently the curves in this region are shown dotted. Where the scale of the graphs permits, the values for $\rho = 1$ obtained with the atomic and molecular wavefunctions are shown separately.

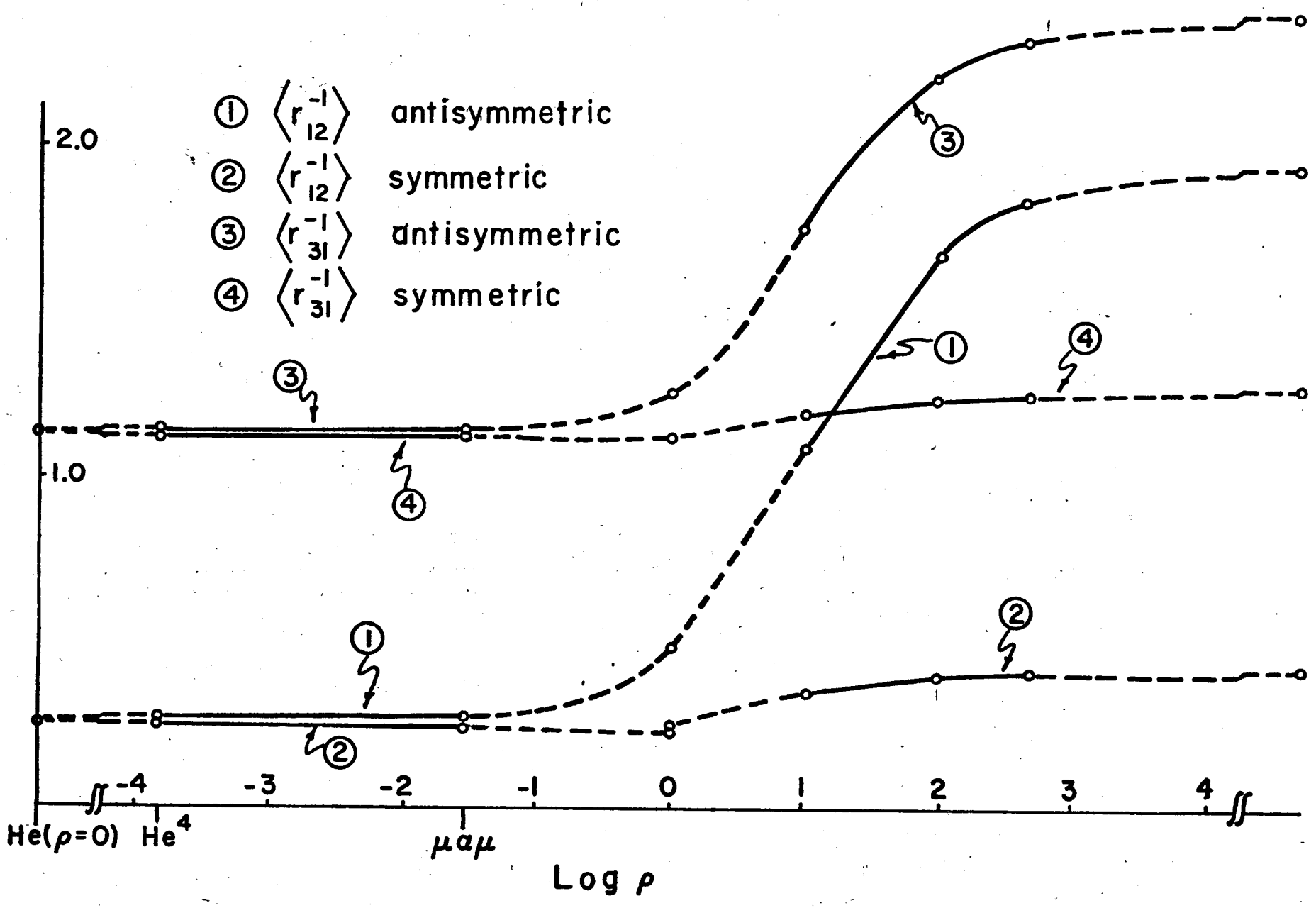
LEGEND FOR FIGURE 6

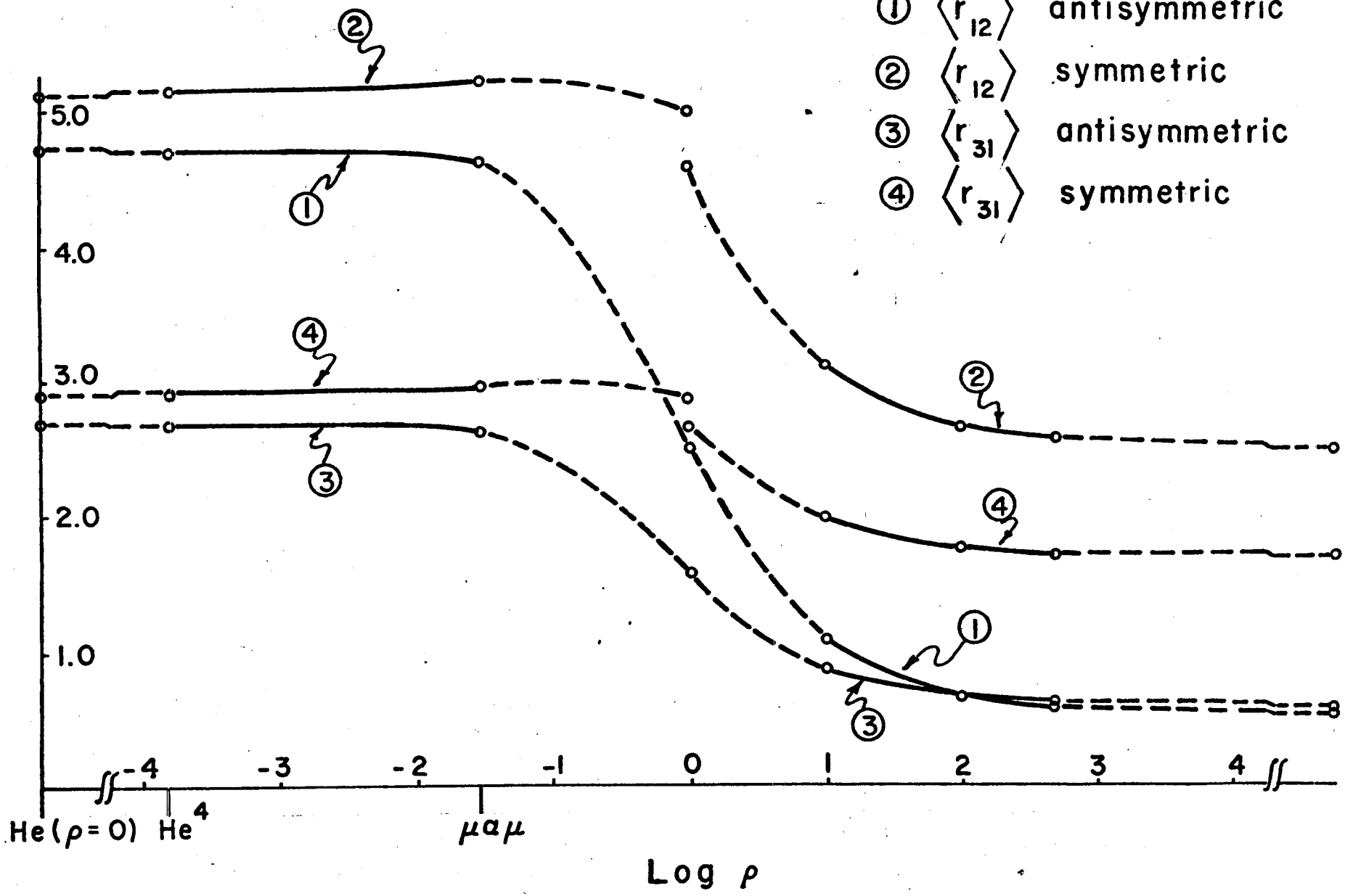
Charge ratio $\sigma = -2$. The expectation values of r_{ij}^2 in reduced atomic units for the symmetric and antisymmetric states as a function of $\lg \rho$. The shape of the curves near $\rho = 1$ is not definitely established from the information given in Tables 2 and 3, and consequently the curves in this region are shown dotted. Where the scale of the graphs permits, the values for $\rho = 1$ obtained with the atomic and molecular wavefunctions are shown separately.

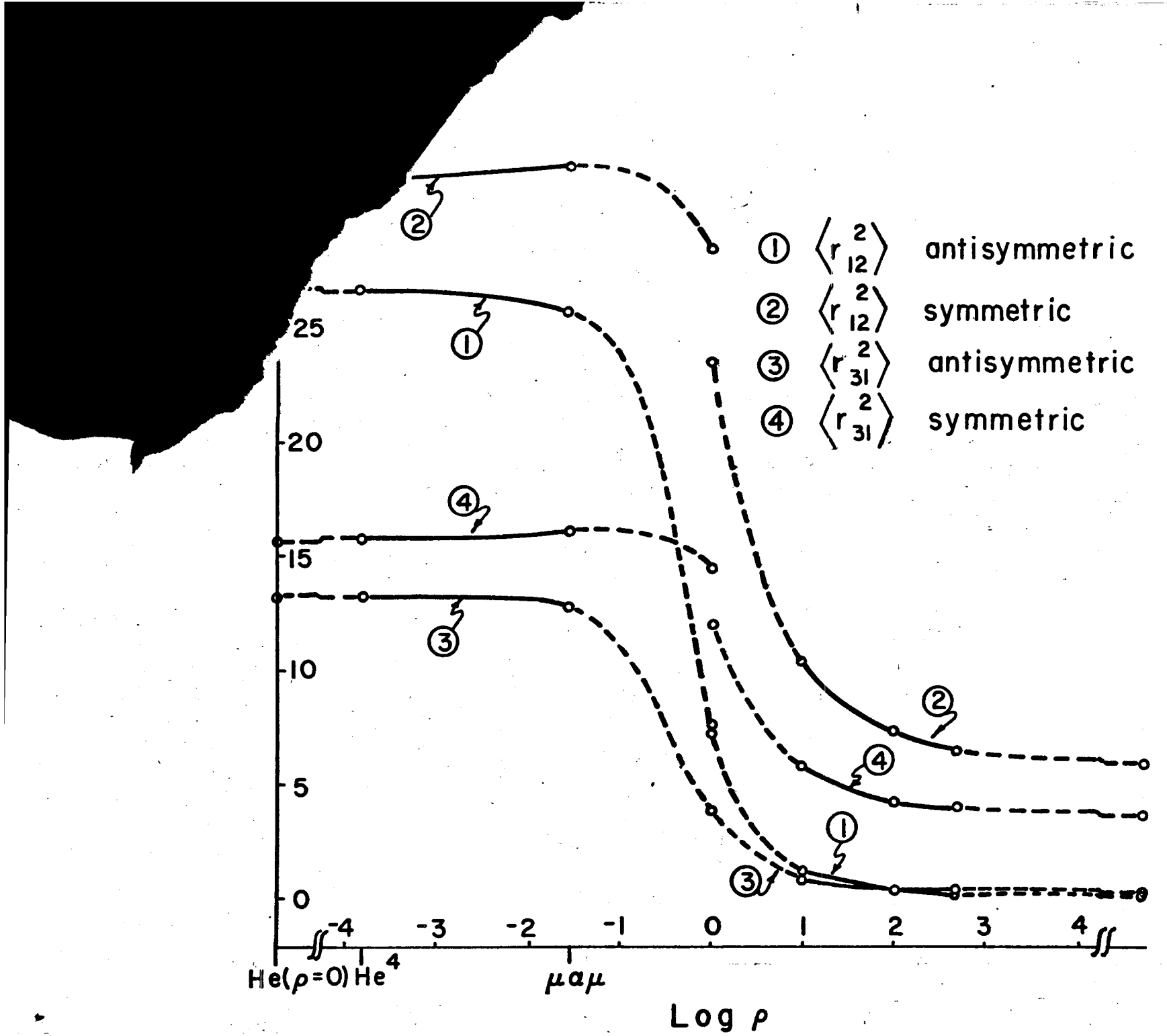

-0.5
dissociation
-0.55
-0.6
Energy (a.u.)
L = 1
L = 0
(ground state)
1
2
3
4
e⁻e⁺e⁻
pμp
dμd
tμt
H₂⁺
D₂⁺
T₂⁺
H₂⁺(∞)
Log ρ


15
10
5
① 10 ⟨r$_{12}^{-1}$⟩
② 10 ⟨r$_{31}^{-1}$⟩
③ ⟨r$_{12}$⟩
④ ⟨r$_{31}$⟩
⑤ ⟨r$_{12}^{2}$⟩
⑥ ⟨r$_{31}^{2}$⟩
1
2
3
4
pμp dμd tμt
H$_2^+$ D$_2^+$ T$_2^+$ H$_2^+$(∞)
Log ρ


-2.0
-3.0
Energy (a.u.)
symmetric
antisymmetric
-4
-3
-2
-1
0
1
2
3
4
He(ρ=0)
He⁴
μaμ
Log ρ


① $\langle r_{12}^{-1} \rangle$ antisymmetric
② $\langle r_{12}^{-1} \rangle$ symmetric
③ $\langle r_{31}^{-1} \rangle$ antisymmetric
④ $\langle r_{31}^{-1} \rangle$ symmetric
2.0
1.0
-4
-3
-2
-1
0
1
2
3
4
He(ρ=0)
He⁴
μaμ
Log ρ


① ⟨r12⟩ antisymmetric
② ⟨r12⟩ symmetric
③ ⟨r31⟩ antisymmetric
④ ⟨r31⟩ symmetric
5.0
4.0
3.0
2.0
1.0
-4
-3
-2
-1
0
1
2
3
4
He(ρ=0)
He⁴
μaμ
Log ρ


① $\langle r_{12}^2 \rangle$ antisymmetric
② $\langle r_{12}^2 \rangle$ symmetric
③ $\langle r_{31}^2 \rangle$ antisymmetric
④ $\langle r_{31}^2 \rangle$ symmetric
25
20
15
10
5
0
-4
-3
-2
-1
0
1
2
3
4
He(ρ=0) He⁴
μαμ
Log ρ